

## FUNCTIONAL PASTE

Field of the Invention

[0001]

5           The invention relates to functional paste having an etching function and conductivity.

Background of the Invention

[0002]

10           At present extensive research has been performed on conductive paste containing a metal powder, because it is used for various purposes including fabrication of electrodes for solar cells, formation of jumper cables using electronic components, e.g., printed-wiring boards, and formation of terminal outgoing lines of printed resistors.

[0003]

15           For example, in the fabrication of surface electrodes of solar cells, conventionally, an antireflection layer formed on a semiconductor layer is patterned using photoresist, then a surface electrode is fabricated (patent reference 1). However, this method is very complicated because it requires two steps: patterning of an antireflection layer, and fabrication of an electrode.

20           To eliminate the patterning process of antireflection layers, a method was proposed, wherein an antireflection layer is formed only on an light absorption side by masking the semiconductor layer during the formation of the antireflection layer which is the process prior to the patterning process. However, this method of direct patterning of antireflection layers has technological difficulties, and is not yet sufficient for practical application. Meanwhile, as a study on the fabrication of surface electrodes of solar cells, 25 a so-called fire-through method has been proposed (patent reference 2), in which after the easy formation of an antireflection layer using a method such as a thermal oxidation method, conductive paste comprising a metal powder and a glass material is printed on the antireflection layer, then the metal powder is in contact with the n- or p-layer silicon of the silicon substrate to form an electrode while the glass material contained in the 30 conductive paste melts the antireflection layer, so that the conduction between the metal electrode and the n- or p-layer silicon can be ensured. However, because this fire-through method requires a baking process generally at a high temperature of 850°C, the glass component and the electrode sometimes penetrate the n-layer, resulting in the deterioration of electrical properties of solar cells; therefore, accurate control of the 35 fabrication conditions is necessary. In addition, when there is no uniform conduction between the electrode and the n-layer silicon, initial electrical properties of solar cells deteriorate, leading to a problem.

Thus, the development of functional paste having a superior etching function and good electrical properties has been strongly desired in the art.

[0004]

Patent reference 1: Patent Application No. 2000-49368

5 Patent reference 2: Patent Application No. 2002-176186

#### Disclosure of the Invention

##### Aims of the Invention

[0005]

10 The invention was performed under the above circumstances, and it provides functional paste which has etching activity and good electrical properties.

##### Summary of the Invention

[0006]

15 Inventors of the invention made extensive examinations to resolve the above issues, and found that during the fabrication process of paste by mixing a metal powder, a binder and an organic solvent, the mixture of an etching agent into the paste enables stable etching of an antireflection layer at a low temperature of approximately 200°C in the fabrication of a surface electrode of a solar cell. The invention was achieved based on this finding.

[0007]

20 Thus, the invention relates to functional paste comprising a metal powder, an etching agent, a binder and an organic solvent.

The invention also relates to the functional paste which further comprises a diluent.

25 The invention also relates to the functional paste wherein the diluent is butylcarbitol.

The invention also relates to the functional paste wherein the etching agent has removal activity of oxidation layers on the surface of the metal powders.

The invention also relates to the functional paste wherein the etching agent has etching activity for antireflection layers of solar cells.

30 The invention also relates to the functional paste wherein the etching agent has removal activity of oxidation layers and/or nitride layers of Si.

The invention also relates to the functional paste wherein the etching agent is  $\text{NH}_4\text{HF}_2$  or  $\text{NH}_4\text{F}$ .

[0008]

35 Furthermore, the invention relates to the functional paste wherein the metal powder is one or more powder selected from the group consisting of Ag-coated Ni powder, Cu powder, Ag powder, Au powder, Pd powder and Pt powder.

The invention also relates to the functional paste wherein the binder contains a thermosetting resin.

The invention also relates to the functional paste wherein the thermosetting resin is an epoxy resin and/or phenol resin.

5 The invention also relates to the functional paste wherein the organic solvent is polyhydric alcohol or its mixture.

The invention also relates to the functional paste wherein the polyhydric alcohol is glycerin and/or ethylene glycol.

[0009]

10 Furthermore, the invention relates to a solar cell comprising a semiconductor layer, an antireflection layer above the semiconductor layer, and a surface electrode which penetrates through the antireflection layer to bring the semiconductor layer into conduction, wherein the solar cell is fabricated by coating and baking the functional  
15 paste comprising a metal powder, an etching agent having etching activity for antireflection layers, a binder and an organic solvent, on the antireflection layer in a desired electrode shape.

The invention also relates to an electric circuit formed by coating and baking the functional paste comprising a metal powder, an etching agent having removal activity of oxidation layers on the surface of the metal powders, a binder and an organic solvent,  
20 on a substrate in a desired pattern.

[0010]

Furthermore, the invention relates to a method of fabricating a solar cell comprising a semiconductor layer, an antireflection layer above the semiconductor layer, and a surface electrode which penetrates through the antireflection layer to bring the  
25 semiconductor layer into conduction, wherein the method comprises coating and baking the functional paste comprising a metal powder, an etching agent having etching activity for antireflection layers, a binder and an organic solvent, on the antireflection layer in a desired electrode shape.

The invention also relates to a method of forming electric circuits, which  
30 comprises coating and baking the functional paste comprising a metal powder, an etching agent having removal activity of oxidation layers on the surface of the metal powders, a binder and an organic solvent, on a substrate in a desired pattern.

### Utility of the Invention

[0011]

According to the invention, an etching agent contained in the paste enables  
5 stable removal of an antireflection layer under a low temperature without penetrating the  
n-layer for the fabrication of electrodes of solar cells, thus achieving easy, single-step  
fabrication of surface electrodes with a low interface resistance.

The invention also enables stable and single-step fabrication of surface  
electrodes at a low temperature of approximately 200°C, thus significantly simplifying  
10 the fabrication process. Therefore, by the simple replacement of conventional materials  
with the functional paste of the invention, the cost and yield can be markedly improved,  
which provides significant contribution to the art.

Furthermore, because a thin natural oxidation layer is formed on the surface of  
metal powders of paste due to water or oxygen, sometimes stable electric conduction  
15 may not be obtained. However, with the functional paste according to this invention, the  
etching agent also removes such oxidation layers, and thus, the formation of an electric  
circuit with extremely small resistance is achieved.

### Preferred Embodiment of the Invention

[0012]

20 The following is a detailed explanation of the invention.

As a metal powder of the functional paste of the invention, a Ag-coated Ni powder,  
Cu powder, Ag powder, Ni powder and Al powder are used. Among them, a Ag-coated Ni  
powder, Cu powder and Ag powder are preferred from the viewpoint of soldering  
characteristics. The contents of the metal powder relative to the total weight of the  
25 functional paste are, preferably 60-99 wt.%, and more preferably 65-90 wt.%.

[0013]

As an etching agent of the functional paste of the invention, bifluoride such as  
 $\text{NH}_4\text{HF}_2$  and  $\text{NH}_4\text{F}$  is used; among them,  $\text{NH}_4\text{HF}_2$  is preferred from the viewpoint of  
reactivity. The contents of the etching agent relative to the total weight of the functional  
30 paste are, preferably 0.1-20 wt.%, and more preferably 1-10 wt.%.

[0014]

As a thermosetting resin contained in the binder of the functional paste of the  
invention, an epoxy resin, phenol resin, polyimide resin and polycarbonate resin are used.  
Among them, an epoxy resin and phenol resin are preferred from the viewpoint of coating  
35 characteristics. The contents of the thermosetting resin relative to the total weight of the  
functional paste are, preferably 0.1-30 wt.%, and more preferably 1-10 wt.%.

In the binder, a hardener such as dicyandiamide and fatty polyamine is added; among them, dicyandiamide is preferred. The contents of the hardener relative to the total weight of the functional paste are, preferably 0.1-30 wt.%, and more preferably 1-20 wt.%.

5 In the binder, a hardening accelerator such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea and tertiary amine is further added; among them, 3-(3,4-dichlorophenyl)-1,1-dimethylurea is preferred. The contents of the hardening accelerator relative to the total weight of the functional paste are, preferably 0.01-10 wt.%, and more preferably 0.1-7.0 wt.%.

10 [0015]

As an organic solvent of the functional paste of the invention, any organic solvent which can homogeneously disperse the bifluoride, i.e., an inorganic salt, in the functional paste, can be used, for example, polyhydric alcohol such as glycerin, ethylene glycol, glucitol and mannitol, or their mixture. Among them, glycerin and ethylene glycol are  
15 preferred from the viewpoint of reactivity. The contents of the organic solvent relative to the total weight of the functional paste are, preferably 0.1-30 wt.%, and more preferably 1-20 wt.%.

Furthermore, in the functional paste of the invention, a diluent such as butyl carbitol, methyl carbitol, solubesso(?)150 may be added to adjust the viscosity to be applicable to  
20 screen printing (approximately 200-500 poise). Among these diluents, butyl carbitol is preferred. The contents of the diluent relative to the total weight of the functional paste are, preferably 0.1-10 wt.%, and more preferably 0.5-7 wt.%.

[0016]

In order to improve the electrical contact between metal powders, a colloidal  
25 solution such as a silver colloidal solution AgE-102 (Nippon Paint Co., Ltd.) and DCG (Sumitomō Metal Mining Co., Ltd.) may be added to the functional paste of the invention. The contents of the colloidal solution in terms of Ag-converted amount relative to the total weight of the functional paste are, preferably 1.0-20 wt.%, and more preferably 1.5-15 wt.%.

30 [0017]

Furthermore, in order to promote the breakage of an oxidation layer on the surface of the metal powder, unsaturated fatty acid such as oleic acid and linoleic acid may be diluted in the functional paste of the invention. The contents of the unsaturated fatty acid relative to the total weight of the functional paste are, preferably 0.1-5.0 wt.%, and more  
35 preferably 0.5-3.0 wt.%.

[0018]

The functional paste of the invention with the above composition can be, after thorough mixture of the paste using, e.g., a hybrid mixer until homogeneous dispersion is achieved, painted in a desired shape using various methods including printing, spraying and brush painting. Subsequently, after drying at a temperature of 30-80°C, an electric circuit can be easily formed by baking at a temperature of 150-250°C for 5-20 min.

[0019]

An example of the fabrication method of electrodes of solar cells using the functional paste of the invention is explained (Fig. 1). First, n-type impurities are dispersed on a p-type silicon substrate to form an n-type region (n+ layer). Next, an antireflection layer ( $\text{SiO}_2$ ,  $\text{SiN}_x$ ) is formed on the n-type region, which becomes an acceptance surface, using, e.g., a CVD device; then a p+ layer, which is a region for the dispersion of high-concentration p-type impurities, is formed on the opposite surface of the acceptance surface.

Then, after attachment and drying of the functional paste of the invention in a desired electrode shape using, e.g., a screen printing method, the paste is baked on the antireflection layer, so that a surface electrode which achieves good electric conduction with the n-layer silicon can be fabricated while etching the antireflection layer. The functional paste of the invention has both functions of the etching reaction for antireflection layers and the electric conduction; therefore, surface electrodes can be easily fabricated by a single step. Finally, by the formation of a back-surface electrode underneath the p+ layer, a solar cell with superior electrical properties can be obtained.

[0020]

The following examples are provided for detailed illustrative purposes and are not intended to restrict the invention.

#### Example 1

A mixture of

Ag-coated Ni powder: 93 parts by weight (75.0 wt.%),

oleic acid: 1 part by weight (0.8 wt.%),

epoxy resin: 6 parts by weight (4.8 wt.%),

ammonium hydrogen fluoride: 3 parts by weight (2.4 wt.%), and

butyl carbitol: 6 parts by weight (4.8 wt.%),

prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1 weight ratio in an amount of 15 parts by weight (12.1 wt.%), well mixed, and the resultant was applied on a Si wafer with a width approximately 1 mm, length approximately 1 cm, and thickness approximately 400  $\mu\text{m}$ , then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min, so that an electrode was formed. The resistance between the two electrodes was 90  $\Omega$ .

The preparation of the above composition excluding the ammonium hydrogen fluoride was used to form an electrode using the same process. The resistance between the two electrodes was 210 k $\Omega$ .

[0021]

5 Example 2

A mixture of

Ag-coated Ni powder: 93 parts by weight (75.0 wt.%),

oleic acid: 1 part by weight (0.8 wt.%),

epoxy resin: 6 parts by weight (4.8 wt.%),

10 ammonium hydrogen fluoride: 3 parts by weight (2.4 wt.%), and

butyl carbitol: 6 parts by weight (4.8 wt.%),

prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1

weight ratio in an amount of 15 parts by weight (12.1 wt.%), well mixed, and the resultant

was applied on a Si wafer having a SiO<sub>2</sub> layer of approximately 80 nm thickness, with a

15 width approximately 1 mm, length approximately 1 cm, and thickness approximately 400

$\mu$ m, then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15

min, so that an electrode was formed. The resistance between the two electrodes was 900  $\Omega$ .

The preparation of the above composition excluding the ammonium hydrogen

20 fluoride was used to form an electrode using the same process. The resistance between the two electrodes was 100 M $\Omega$  or greater.

[0022]

Example 3

A mixture of

25 Ag-coated Ni powder: 93 parts by weight (66.9 wt.%),

oleic acid: 1 part by weight (0.7 wt.%),

epoxy resin: 6 parts by weight (4.3 wt.%),

ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and

butyl carbitol: 6 parts by weight (4.3 wt.%),

30 prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1

weight ratio in an amount of 15 parts by weight (10.8 wt.%) and a silver colloidal solution

AgE-102 (Nippon Paint Co., Ltd.) in an amount of 15 parts by weight (10.8 wt.%), well

mixed, and the resultant was applied on a Si wafer having a SiO<sub>2</sub> layer, with a width

approximately 1 mm, length approximately 1 cm, and thickness approximately 400  $\mu$ m,

35 then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min,

so that an electrode was formed. The resistance between the two electrodes was 160  $\Omega$ .

The preparation of the above composition excluding the silver colloidal solution AgE-102 was used to form an electrode using the same process. The resistance between the two electrodes was 550  $\Omega$ .

[0023]

5 Example 4

A mixture of

Ag-coated Ni powder: 93 parts by weight (66.9 wt.%),

oleic acid: 1 part by weight (0.7 wt.%),

epoxy resin: 6 parts by weight (4.3 wt.%),

10 ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and

butyl carbitol: 6 parts by weight (4.3 wt.%),

prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1 weight ratio in an amount of 15 parts by weight (10.8 wt.%) and a silver colloidal solution

AgE-102 (Nippon Paint Co., Ltd.) in an amount of 15 parts by weight (10.8 wt.%), well

15 mixed, and the resultant was applied on a Si wafer having a SiN<sub>x</sub> layer of approximately 90 nm thickness, with a width approximately 1 mm, length approximately 1 cm, and thickness approximately 400  $\mu$ m, then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min, so that an electrode was formed. The resistance between the two electrodes was 1.9 k $\Omega$ .

20 The preparation of the above composition excluding the mixture of glycerin/ethylene glycol = 3/1 weight ratio was used to form an electrode using the same process. The resistance between the two electrodes was 29 k $\Omega$ .

[0024]

Example 5

25 A mixture of

Ag-coated Ni powder: 93 parts by weight (66.9 wt.%),

oleic acid: 1 part by weight (0.7 wt.%),

epoxy resin: 6 parts by weight (4.3 wt.%),

ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and

30 butyl carbitol: 6 parts by weight (4.3 wt.%),

prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1 weight ratio in an amount of 15 parts by weight (10.8 wt.%) and a silver colloidal solution AgE-102 (Nippon Paint Co., Ltd.) in an amount of 15 parts by weight (10.8 wt.%), well mixed, and the resultant was applied on a Si wafer with a width approximately 1 mm,

35 length approximately 1 cm, and thickness approximately 400  $\mu$ m, then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min, so that an electrode was formed. The resistance between the two electrodes was 0  $\Omega$ .



The preparation of the above composition excluding the mixture of glycerin/ethylene glycol = 3/1 weight ratio was used to form an electrode using the same process. The resistance between the two electrodes was 9.3  $\Omega$ .

[0025]

5 Example 6

A mixture of

Cu powder: 93 parts by weight (66.9 wt.%),

oleic acid: 1 part by weight (0.7 wt.%),

epoxy resin: 6 parts by weight (4.3 wt.%),

10 ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and

butyl carbitol: 6 parts by weight (4.3 wt.%),

prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1 weight ratio in an amount of 15 parts by weight (10.8 wt.%) and a silver colloidal solution AgE-102 (Nippon Paint Co. Ltd.) in an amount of 15 parts by weight (10.8 wt.%), well

15 mixed, and the resultant was applied on a Si wafer of approximately 80 nm thickness, with a width approximately 1 mm, length approximately 1 cm, and thickness approximately 400  $\mu\text{m}$ , then baked on a hot plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min, so that an electrode was formed. The resistance between the two electrodes was 10 k $\Omega$ .

20 The preparation of the above composition excluding the ammonium hydrogen fluoride was used to form an electrode using the same process. The resistance between the two electrodes was 2 M $\Omega$ .

Example 7

A mixture of

25 Ag-coated Ni powder: 90 parts by weight (66.7 wt.%),

oleic acid: 1 part by weight (0.7 wt.%),

phenol resin: 9 parts by weight (6.7 wt.%),

ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and

butyl carbitol: 2 parts by weight (1.5 wt.%),

30 prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1 weight ratio in an amount of 15 parts by weight (11.1 wt.%) and a silver colloidal solution AgE-102 (Nippon Paint Co. Ltd.) in an amount of 15 parts by weight (11.1 wt.%), well mixed, and the resultant was applied on a Si wafer, with a width approximately 5 mm, length approximately 5 mm, and thickness approximately 200  $\mu\text{m}$ , then baked on a hot  
35 plate in air at 70-75°C for 5 min and subsequently at 220°C for 15 min, so that an electrode was formed. The resistance between the two electrodes was 34 k $\Omega$ .

The preparation of the above composition excluding the ammonium hydrogen fluoride and Ag-coated Ni powder-102 was used to form an electrode using the same process. The resistance between the two electrodes was 730 k $\Omega$ .

#### Example 8

- 5 A mixture of  
Ag-coated Ni powder: 90 parts by weight (66.7 wt.%),  
oleic acid: 1 part by weight (0.7 wt.%),  
phenol resin: 9 parts by weight (6.7 wt.%),  
ammonium hydrogen fluoride: 3 parts by weight (2.2 wt.%), and  
10 butyl carbitol: 2 parts by weight (1.5 wt.%),  
prepared using a hybrid mixer was added with a mixture of glycerin/ethylene glycol = 3/1  
weight ratio in an amount of 15 parts by weight (11.1 wt.%) and a silver colloidal solution  
AgE-102 (Nippon Paint Co. Ltd.) in an amount of 15 parts by weight (11.1 wt.%), well  
mixed, and the resultant was applied on a Si wafer having a SiO<sub>2</sub> layer of approximately  
15 80  $\mu$  m thickness,, with a width approximately 5 mm, length approximately 5 mm, and  
thickness approximately 200  $\mu$  m, then baked on a hot plate in air at 70-75°C for 5 min and  
subsequently at 220°C for 15 min, so that an electrode was formed. The resistance  
between the two electrodes was 12 k $\Omega$ .

- The preparation of the above composition excluding the ammonium hydrogen  
20 fluoride and Ag-coated Ni powder-102 was used to form an electrode using the same  
process. The resistance between the two electrodes was 10 M $\Omega$  or more than.

[0026]

The functional paste of the invention can be used for the fabrication of surface  
electrodes of solar cells and for the formation of electric circuits.

#### 25 Brief Description of the Drawings

[0027]

Figure 1 shows a method for the fabrication of electrodes of solar cells.

#### Description of Symbols

[0028]

- 30 1: p-type silicon substrate  
2: n+ layer  
3: antireflection layer (SiO<sub>2</sub>, SiN<sub>x</sub>)  
4: p+ layer  
5: surface electrode  
35 6: back-surface electrode